

A NOVEL METHOD FOR THE DETERMINATION OF THE BOILING RANGE OF LIQUID FUELS BY THERMOGRAVIMETRIC ANALYSIS

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INTRODUCTION

The most widely used separation technique in the petroleum industry as well as in much of the chemical industry is distillation. This is particularly true of all liquid fuel production processes, including coal-derived liquid fuels, and shale oil as well as petroleum. To design and operate a suitable distillation column system requires a knowledge of the boiling point distribution of the materials to be separated. In recognition of this need, the ASTM developed the classical distillation procedures of ASTM D86, D216, D447, D850, and D1078. Since these methods required a relatively large sample and are not particularly precise, the widely used simulated distillation analysis based on gas chromatography (ASTM D3710-83) was introduced. This method requires only a small sample size and is reasonably rapid. However, it is limited to materials boiling below about 350°C. Above that temperature the column packing becomes unstable and the materials being analyzed tend to crack. Also the results measured by the SimDis GC method are determined by the interactions between the tested sample and the selected column packing. Therefore the GC method is not fundamentally a determination of the boiling range of the sample mixture but rather a measure of the range of interactions of the sample with the packing.

To avoid the limitation in the higher boiling range of the tested material in the SimDis GC method, Schwartz et al developed a capillary supercritical fluid chromatography (SFC) method (1). When the SFC is properly calibrated, it has been shown to be a suitable simulated distillation method, even for materials having atmospheric equivalent boiling points as high as 760 °C or 1400 °F. However this does not eliminate the problem of interactions of the sample with the packing material.

In their work, Schwartz et al also used both atmospheric "flow" thermogravimetric analysis (FTGA) and vacuum thermogravimetric analysis (VTGA) methods to distinguish between evaporation and thermal decomposition. They have observed a bimodal distribution of DTG (the rate of weight loss) on Arabian heavy atmospheric residue in both FTGA and VTGA runs. The first peak in the VTGA (about 0.2-0.5 torr) profile is shifted towards lower temperature as compared with the FTGA profile since the sample vaporization was enhanced by a reduced pressure. However, the reduced pressure had no effect on the position of the second peak in the VTGA curve since the thermal decomposition or pyrolysis rate was not significantly affected by the reduced pressure. Therefore, the low temperature peak in each DTG curve is interpreted as the sample vaporization profile and the high temperature peak as the thermal decomposition or pyrolysis reactions.

In the investigation of the hydrocracking of high boiling coal derived vacuum resids, it became important to measure the degree to which the resids had been broken down to lower boiling products. This plus the importance of a simple, rapid, and accurate analytical distillation technique mentioned above motivated the development of an analytical TGA method for boiling range measurement, i.e. atmospheric equivalent boiling point (AEBP) curve, of a variety of samples. While supercritical chromatography was an alternative, the use of thermogravimetric analysis to determine the AEBP curve was an attractive approach. Such a SimDis TGA method would not be affected by interactions with column packing and not limited by sample boiling point range. Development of this novel SimDis TGA method and the preliminary results on a variety of samples are presented in this paper.

EXPERIMENTAL

TGA Apparatus. A horizontal thermogravimetric analyzer (TGA), TA Instruments model 51 (New Castle, Delaware), was used. In this particular instrument, dual thermocouples were used for the system temperature control. One is a furnace thermocouple and the other is a sample thermocouple, which is located very close to the test sample. The sample thermocouple is always used for the temperature measurements. Only the furnace thermocouple is used for control in the ramp method (constant heating rate). However, either the furnace thermocouple or the sample thermocouple can be used for isothermal control, depending on the purpose. If the "Isothermal" mode is selected, the

furnace thermocouple is used. On the other hand, if the "Isotrack" mode is selected, the sample thermocouple is used. The isotrack mode gives much better temperature control, for example, ± 0.01 to ± 0.05 °C for the range of 60 to 280 °C, compared to the Isothermal mode.

Nitrogen was used as an inert carrier gas at 100 ml/min volumetric flow rate. Vacuum TGA (VTGA) was carried out by attachment of the thermogravimetric analyzer to a vacuum pump. A vacuum gauge from 0-760 mmHg (0-1 atm.) range was used to monitor the pressure. After a sample was loaded onto the sample pan, the vacuum metering valve (shown in Figure 1) was gradually opened, and the pressure was adjusted to a predetermined value (down to 30 mmHg or 0.0395 atm). By this control and use of a ballast tank (buffer), the pressure (or vacuum) of the TGA chamber was found to be very stable during the VTGA analysis.

TGA Sample Pan. The SimDis TGA method requires a change in the conventional TGA sample pan because the rate of weight loss in the open pan system is controlled not only by the vapor pressure of the test sample but also by mass transfer. The TGA sample characteristics in the pan as well as the diffusion out constantly change with the sample amount as the TG analysis proceeds. For those reasons, a new sample pan configuration with a small aperture at the top, as shown in Figure 2, was devised. The objective of this change is to make the rate of the weight loss from the sample pan primarily determined by the partial pressure of the sample molecules. This partial pressure has been shown from thermodynamic considerations and experimentation to be essentially equal to the vapor pressure of the sample. Three cylindrical quartz TGA sample pans with different sizes of circular aperture at the top were fabricated. The diameters of the apertures were 0.615, 0.974, and 1.538 mm. In each TGA test, about 80 mg of liquid sample was injected into the sample pan by a syringe before the TG analysis.

SimDis TGA Methods. Analytical variables, such as carrier gas flow rate, pressure, and temperature or heating rate, were held constant during a TG analysis. Two methods, i.e., a ramp method and an isotrack method, have been used in the SimDis TGA technique. In the ramp method, a constant heating rate was used and the rate of the weight loss determined versus temperature. In the isotrack method, the temperature of the sample is very rapidly heated to a predetermined temperature within 2 minutes, and precisely controlled at this preset temperature within 0.01 to 0.05 °C after 5 minutes. The weight change and the DTG (the differential of the weight loss curve) decay are determined as a function of time.

Materials Studied. A light paraffinic vacuum distillate from Amoco and a converted resid liquid were used to test the SimDis TGA technique.

SimDis TGA Calibration. A SimDis TGA system can be calibrated by either a synthetic mixture which contains compounds of known boiling range or a 'standard' mixture for which distillation curves are available. In either case, the calibration sample should be similar to the sample for which the boiling range is to be determined. For the synthetic mixture, the paraffins, especially n-alkanes, provide a wide range of boiling components for calibration purposes. For the 'standard' mixture, any petroleum sample with known boiling range distribution could be selected. Some variation between samples of the same boiling point but different chemical structure are to be expected due to variation in molecular characteristics (such as molecular weight and shape) and heats and entropies of vaporization of the samples.

n-Alkane standards, C-10 to C-32, were purchased from Aldrich Chemical Co (Milwaukee, NJ). The SimDis TGA was calibrated with a synthetic mixture of these n-alkane standards shown in Table 1.

SimDis TGA Data Processing. The smoothed and noise-free DTG curves were acquired by an 11 point smoothing technique (2).

RESULTS AND DISCUSSION

Strategies for Selection of the Optimum Method for Determining Boiling Point Range of an Unknown Sample. The analytical variables of the SimDis TGA technique include: 1). time-temperature profile: ramp method or isotrack method; 2). pressure: atmospheric pressure or under vacuum (down to 0.03 atm.); 3). size of the aperture at the top of the pan; and 4). carrier gas type and flow rate.

For a pure compound, SimDis TGA can be run using either the ramp or isotrack method. For an unknown mixture, the ramp method provides information concerning the vaporization range of the sample. If run under at least two pressures (vacuum), it can distinguish quantitatively between the material boiling so high that pyrolysis will occur and that fraction volatilizing under distillation conditions.

To accurately obtain the boiling range curve for a mixture, the isotrack method is the preferred technique. This method translates the decay of the rate of weight loss into the boiling point distribution. Therefore, the optimum conditions to run a simulated distillation by TGA are those conditions which give the highest sensitivity and stable decay curve. To accomplish this, the optimum conditions for a SimDis TGA run is dependent on the boiling range of the test sample. For example, for light samples, it is better to run the SimDis TGA at a low isotrack temperature, small hole size of pan, and atmospheric pressure. For very high boiling mixtures, SimDis TGA should be run at a higher isotrack temperature, larger hole size of pan, and high vacuum (for example, 30 mmHg). For a mixture containing a very broad boiling range, the test can be run at either more than one temperature or more than one pressure (vacuum) or both to detect the very volatile fraction as well as the higher boiling components.

The recommended general steps to run an unknown sample using the SimDis TGA technique are:

- 1). ramp at 1 to 5 °C/min to 600 °C at 1 atm and/or under vacuum (down to ca. 0.03 atm.) at 100 cm³/min N₂. Oxygen is then introduced to burn off the combustible material remaining (if any). In this run, IBP (Initial Boiling Point), FBP (Final Boiling Point) and/or PT (Pyrolysis Temperature), the boiling range and volatile fraction, and ash fraction (if any) are determined.
- 2). based on the results obtained from Step 1, select the optimum conditions of aperture size of pan, isotrack temperature, pressure, etc. to run a SimDis TGA.

SimDis TGA by the Ramp Method. Typical DTG curves from SimDis TGA runs using the ramp method at two pressures on a light paraffinic vacuum distillate from Amoco are shown in Figure 3. The rate-of-weight-loss curves show a distinct shift to lower temperatures as the pressure is reduced. No pyrolysis is evident in this determination since the DTG curve is entirely shifted under vacuum. The volatilization range for this sample at atmospheric pressure is between about 200°C and 470 °C. Under the vacuum of 0.238 atm., it is shifted to between about 180°C and 420 °C. The volatilization ranges are somewhat lower than the actual boiling range because of the nitrogen gas sweep and controlled diffusion.

SimDis TGA Calibration. Temperature-time plot for a calibration run using a synthetic mixture of hydrocarbons of C₁₀ to C₃₂ is shown in Figure 4. The predetermined isotrack temperature was 280 °C. The DTG decay curve for this calibration is shown in Figure 5. Although the temperature of the sample reached the predetermined temperature of 280 °C within 2 minutes, the loss of the light fractions in the synthetic mixture, such as C₁₀ and C₁₅, occurred before the temperature became stable. In other words, the light fractions in the synthetic mixture of C₁₀ and C₁₅ were evolved from the sample pan within this initial 2-5 minutes. This is clearly illustrated in Figures 6 and 7, the plot of wt% of sample in the pan vs. temperature and wt% of sample in the pan vs. DTG decay, respectively. From the concentrations of the C₁₀-C₃₂ components in the synthetic mixture given in Table 1, we can find the rates of weight loss at which the components were evolved from the pan. The plot which describes a linear relationship of log (rate of weight loss) vs 1/T_b (T_b, the boiling point of C₂₀-C₃₂) is shown in Figure 8, in accordance with the Clausius-Clapeyron equation. This shows that the DTG decay determined by TGA technique is indeed measuring the vapor pressure and therefore boiling range.

SimDis TGA Test. For a mixture containing a wide range of boiling materials, such as the light paraffinic vacuum distillate from Amoco, the DTG decay determined under the same conditions of running the calibration mixture can be translated into a boiling range distribution using the equation of

$$T_b = \frac{B}{\ln(r) - A} \quad (1)$$

where *r* is the decay rate of the test sample and *A* and *B* are parameters determined by calibration (for this case, *A* = -21.06 and *B* = 12778).

Temperature-time plot for the test sample of the light paraffinic vacuum distillate is similar to that as shown in Figure 4. The DTG decay curve is shown in Figure 9. Although the temperature of the sample reached the predetermined temperature of 280 °C within 2 minutes, the 10 wt% of light fractions in the vacuum distillate were lost before the temperature became stable, i.e., the 10 wt% of light fractions in the vacuum distillate were evolved from the pan within this initial 2-5 minutes. This is clearly illustrated in Figure 10, the plot of wt% of sample in the pan vs. temperature. The simulated distillation curve for this vacuum distillate is shown in Figure 11.

A simulated distillation run by the isotrack method has been made on a sample of Wilsonville # 258 resid converted using sulfided molybdenum naphthenate at 403°C for 60 minutes. The boiling range curve derived from the DTG decay of this sample is shown in Figure 12. The fraction of material in which the product boiled below 850 °F (the cut-off point for resid) was 93.8 wt% (including tetralin fraction).

Advantages of the SimDis TGA Method. The most significant advantages to using the TGA technique for simulated distillation are:

- 1). SimDis TGA is run at much lower temperature than other techniques, especially if combined with vacuum.
- 2). there is no limitation to the sample type. The sample can be very light or very heavy. Even a sample with a very wide range of boiling materials can be tested by this technique.
- 3). Highly reproducible results can be obtained. The experimental cycle for one run can be 1 to 12 hrs, depending on sample and purpose. No cleaning is required as would be necessary in a distillation column.
- 4). Very small amounts of sample (30-80 mg) are required for each SimDis TGA run;
- 5). The SimDis TGA method measures the true boiling characteristics of the sample and is not affected by interactions between the test sample and packing, as is the case with the chromatographic methods.

SUMMARY AND CONCLUSIONS

1. Two analytical methods (a ramp and an isotrack method) have been developed for determining the boiling range of an unknown sample based on the use of thermogravimetric analysis.

2. These methods require the use of a special cylindrical sample pan with a small hole in the top to control the rate of weight loss (diffusion of the sample vapors exiting the pan). Under these conditions, the diffusion rate is proportional to the vapor pressure of the sample at the particular temperature of the analysis.

3. For screening an unknown sample, the "ramp method" is used in which the temperature of the sample is increased at a predetermined rate while holding the purge gas flow rate constant. The temperature range of volatilization is measured. If high boiling material is present which involves pyrolysis of the sample rather than only volatilization, a similar "ramp method" is run under vacuum. This indicates which portion of the sample is volatilized and what portion is pyrolyzed under the conditions of the test.

4. For more precise determination of the boiling range of a sample, the isotrack method is used. In this method, the sample is rapidly heated to a predetermined temperature and then held constant while the rate of weight loss (DTG) is measured. When the system is properly calibrated with a known sample, the rate of weight loss (DTG decay) can be translated by a computer program into an actual boiling range.

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REFERENCES

1. Schwartz, H.E.; Brownlee, R.G.; Boduszynski, M.; Su, F. *Anal. Chem.* 1987, 59, 1393.
2. Wang, Keyu; Huang, H.; Wang, S.; Klein, M.T.; Calkins, W.H. * "A Novel Smoothing Technique for Thermogravimetric Analysis Data", to be submitted to *Anal. Chem.*

Table 1 Concentrations and properties of the C₁₀-C₃₂ components in the synthetic mixture

No. of Carbon	Name	MW	b.p., °C	m.p., °C	W, g	C, wt%
10	Decane	142.28	174.1	-29.7	1.2298	18.26%
15	Pentadecane	212.41	270.6	10.0	1.2068	17.92%
20	Eicosane	282.54	343.0	36.8	1.1238	16.69%
25	Pentacosane	352.67	401.9	55.0	1.0716	15.91%
30	Triacontane	422.80	449.7	65.8	1.0402	15.45%
32	Dotriacontane	450.85	467.0	69.7	1.0618	15.77%

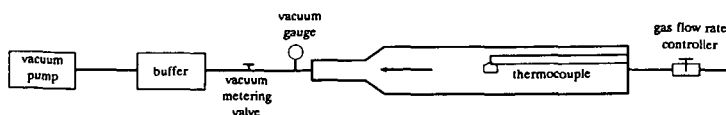


Figure 1 Instrumentation of vacuum thermogravimetric analyzer (VTGA)

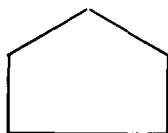


Figure 2 A SimDis TGA sample pan

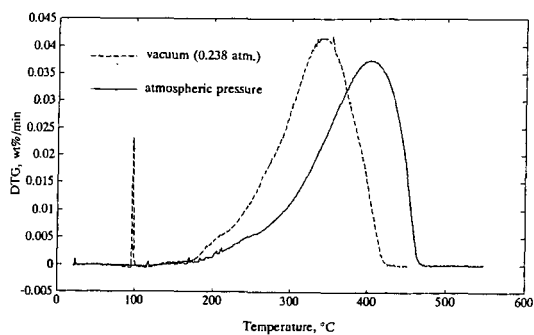


Figure 3 DTG curves from SimDis TGA runs using the ramp method at two pressures on a light paraffinic vacuum distillate from Amoco

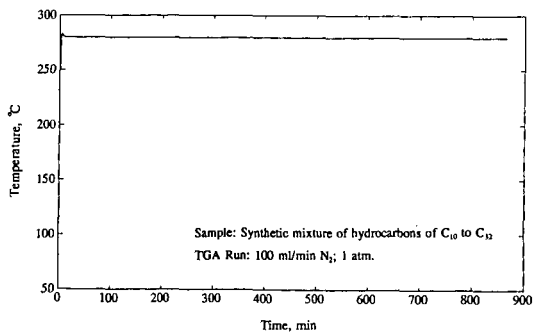


Figure 4 Temperature-time plot for the calibration sample of a synthetic mixture of n-alkanes

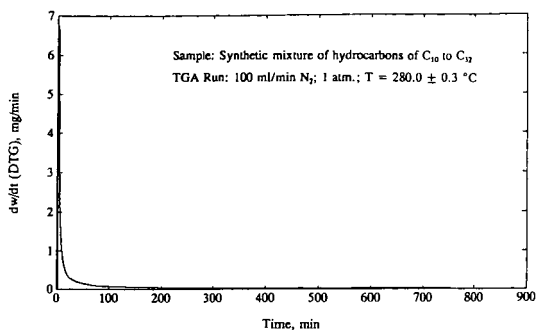


Figure 5 DTG decay curve for the calibration run

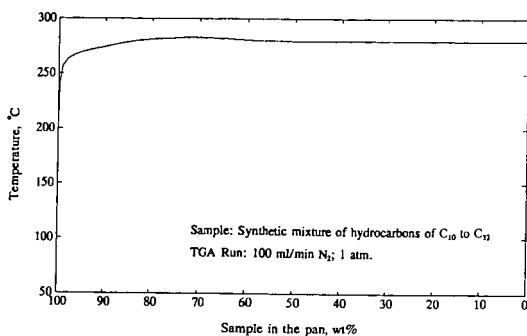


Figure 6 Plot of wt% sample in the pan vs. temperature for the calibration run

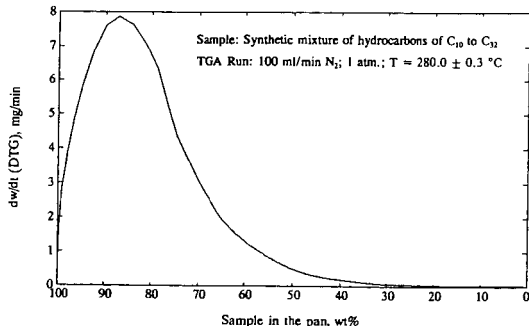


Figure 7 Plot of wt% sample in the pan vs. DTG decay for the calibration run

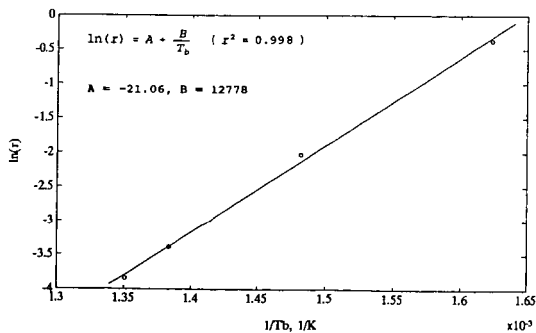


Figure 8 $\ln(r)$ vs. $1/T_b$ (r : rate of weight loss; T_b : boiling point of $C_{20}-C_{30}$)

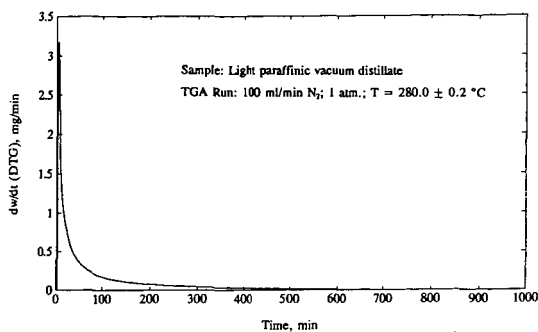


Figure 9 DTG decay curve for the light paraffinic vacuum distillate

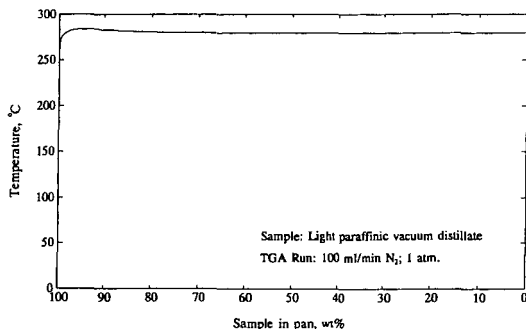


Figure 10 Plot of wt% sample in the pan vs. temperature for the light paraffinic vacuum distillate

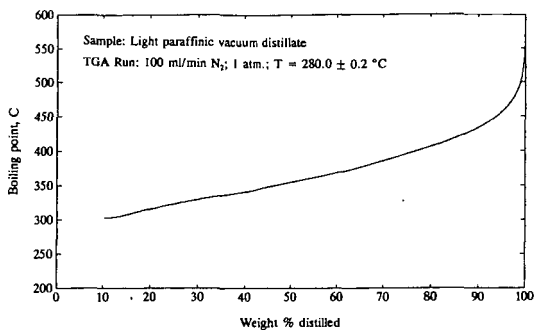


Figure 11 Simulated distillation curve (AEBP) for the light paraffinic vacuum distillate

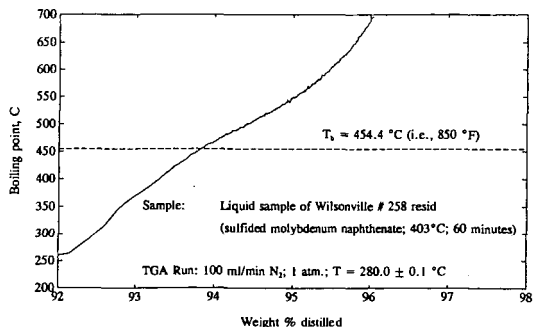


Figure 12 Simulated distillation curve (AEBP) for the liquid sample of a resid conversion run under 1500 psig H_2